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PTO/SB/05 (4/98)
Approved for use through 09/30/2000. OMB 0651-0032
Patent and Trademark Office: U.S. DEPARTMENT OF COMMERCE

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UTILITY PATENT APPLICATION TRANSMITTAL

(Only for new nonprovisional applications under 37 C.F.R. § 1.53(b))

Attorney Docket No.	HRL033B
First Inventor or Application Identifier	Shin-Tson Wu
Title	Polar Tolane Liquid Crystals
Express Mail Label No.	EK030159612US

APPLICATION ELEMENTS

See MPEP chapter 600 concerning utility patent application contents.

ADDRESS TO: **Assistant Commissioner for Patents, Box Patent Application, Washington, DC 20231**

1. [X] * Fee Transmittal Form *(e.g., PTO/SB/17)* *(Submit an original and a duplicate for fee processing)*
2. [X] Specification [*Total Pages* 37] *(preferred arrangement set forth below)*
   - Descriptive title of the Invention
   - Cross References to Related Applications
   - Statement Regarding Fed sponsored R & D
   - Reference to Microfiche Appendix
   - Background of the Invention
   - Brief Summary of the Invention
   - Brief Description of the Drawings *(if filed)*
   - Detailed Description
   - Claim(s)
   - Abstract of the Disclosure
3. [ ] Drawing(s) *(35 U.S.C. 113)* [*Total Sheets*]
4. Oath or Declaration [*Total Pages* 4]
   - a. [X] Newly executed (original or copy)
   - b. [ ] Copy from a prior application (37 C.F.R. § 1.63(d)) *(for continuation/divisional with Box 16 completed)*
     - i. [ ] DELETION OF INVENTOR(S) Signed statement attached deleting inventor(s) named in the prior application, see 37 C.F.R. §§ 1.63(d)(2) and 1.33(b).

** NOTE FOR ITEMS 1 & 13: IN ORDER TO BE ENTITLED TO PAY SMALL ENTITY FEES, A SMALL ENTITY STATEMENT IS REQUIRED (37 C.F.R. § 1.27), EXCEPT IF ONE FILED IN A PRIOR APPLICATION IS RELIED UPON (37 C.F.R. § 1.28).*

5. [ ] Microfiche Computer Program *(Appendix)*
6. Nucleotide and/or Amino Acid Sequence Submission *(if applicable, all necessary)*
   - a. [ ] Computer Readable Copy
   - b. [ ] Paper Copy (identical to computer copy)
   - c. [ ] Statement verifying identity of above copies

ACCOMPANYING APPLICATION PARTS

7. [ ] Assignment Papers (cover sheet & document(s))
8. [ ] 37 C.F.R.§3.73(b) Statement *(when there is an assignee)* [ ] Power of Attorney
9. [ ] English Translation Document *(if applicable)*
10. [ ] Information Disclosure Statement (IDS)/PTO-1449 [ ] Copies of IDS Citations
11. [ ] Preliminary Amendment
12. [X] Return Receipt Postcard (MPEP 503) *(Should be specifically itemized)*
13. [ ] * Small Entity Statement(s) *(PTO/SB/09-12)* [ ] Statement filed in prior application, Status still proper and desired
14. [ ] Certified Copy of Priority Document(s) *(if foreign priority is claimed)*
15. [ ] Other: .....

16. **If a CONTINUING APPLICATION,** *check appropriate box, and supply the requisite information below and in a preliminary amendment.*

[ ] Continuation [ ] Divisional [ ] Continuation-in-part (CIP) of prior application No: _____/_____

Prior application information: *Examiner* _____ *Group / Art Unit:* _____

For CONTINUATION or DIVISIONAL APPS only: The entire disclosure of the prior application, from which an oath or declaration is supplied under Box 4b, is considered a part of the disclosure of the accompanying continuation or divisional application and is hereby incorporated by reference. The incorporation can only be relied upon when a portion has been inadvertently omitted from the submitted application parts.

17. CORRESPONDENCE ADDRESS

[ ] *Customer Number or Bar Code Label* *(Insert Customer No. or Attach bar code label here)* or [X] *Correspondence address below*

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Name (Print/Type)	Cary Tope-McKay	*Registration No (Attorney/Agent)*	41,350
Signature		*Date*	9/1/00

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Patent fees are subject to annual revision.
Small Entity payments must be supported by a small entity statement, otherwise large entity fees must be paid. See Forms PTO/SB/09-12. See 37 C.F.R. §§ 1.27 and 1.28.

TOTAL AMOUNT OF PAYMENT ($) 996

Complete if Known	
Application Number	
Filing Date	
First Named Inventor	Shin-Tson Wu
Examiner Name	
Group / Art Unit	
Attorney Docket No.	HRL033B

METHOD OF PAYMENT (check one)

1. ☐ The Commissioner is hereby authorized to charge indicated fees and credit any overpayments to:

Deposit Account Number

Deposit Account Name

☐ Charge Any Additional Fee Required Under 37 CFR §§ 1.16 and 1.17

2. ☒ **Payment Enclosed:**
☒ Check ☐ Money Order ☐ Other

FEE CALCULATION

1. BASIC FILING FEE

Large Entity Fee Code	Large Entity Fee ($)	Small Entity Fee Code	Small Entity Fee ($)	Fee Description	Fee Paid
101	690	201	345	Utility filing fee	$690
106	310	206	155	Design filing fee	
107	480	207	240	Plant filing fee	
108	690	208	345	Reissue filing fee	
114	150	214	75	Provisional filing fee	

SUBTOTAL (1) ($) 690

2. EXTRA CLAIM FEES

		Extra Claims		Fee from below	Fee Paid
Total Claims	24	-20** =	4	X 18	= 72
Independent Claims	6	- 3** =	3	X 78	= 234
Multiple Dependent				0	= 0

***or number previously paid, if greater; For Reissues, see below*

Large Entity Fee Code	Large Entity Fee ($)	Small Entity Fee Code	Small Entity Fee ($)	Fee Description
103	18	203	9	Claims in excess of 20
102	78	202	39	Independent claims in excess of 3
104	260	204	130	Multiple dependent claim, if not paid
109	78	209	39	** Reissue independent claims over original patent
110	18	210	9	** Reissue claims in excess of 20 and over original patent

SUBTOTAL (2) ($) 306

FEE CALCULATION (continued)

3. ADDITIONAL FEES

Large Entity Fee Code	Large Entity Fee ($)	Small Entity Fee Code	Small Entity Fee ($)	Fee Description	Fee Paid
105	130	205	65	Surcharge - late filing fee or oath	
127	50	227	25	Surcharge - late provisional filing fee or cover sheet.	
139	130	139	130	Non-English specification	
147	2,520	147	2,520	For filing a request for reexamination	
112	920*	112	920*	Requesting publication of SIR prior to Examiner action	
113	1,840*	113	1,840*	Requesting publication of SIR after Examiner action	
115	110	215	55	Extension for reply within first month	
116	380	216	190	Extension for reply within second month	
117	870	217	435	Extension for reply within third month	
118	1,360	218	680	Extension for reply within fourth month	
128	1,850	228	925	Extension for reply within fifth month	
119	300	219	150	Notice of Appeal	
120	300	220	150	Filing a brief in support of an appeal	
121	260	221	130	Request for oral hearing	
138	1,510	138	1,510	Petition to institute a public use proceeding	
140	110	240	55	Petition to revive - unavoidable	
141	1,210	241	605	Petition to revive - unintentional	
142	1,210	242	605	Utility issue fee (or reissue)	
143	430	243	215	Design issue fee	
144	580	244	290	Plant issue fee	
122	130	122	130	Petitions to the Commissioner	
123	50	123	50	Petitions related to provisional applications	
126	240	126	240	Submission of Information Disclosure Stmt	
581	40	581	40	Recording each patent assignment per property (times number of properties)	
146	690	246	345	Filing a submission after final rejection (37 CFR § 1.129(a))	
149	690	249	345	For each additional invention to be examined (37 CFR § 1.129(b))	

Other fee (specify) _____

Other fee (specify) _____

* Reduced by Basic Filing Fee Paid

SUBTOTAL (3) ($) 0

SUBMITTED BY				Complete (if applicable)	
Name (Print/Type)	Cary Tope-McKay	Registration No. (Attorney/Agent)	41,350	Telephone	(310) 589-8158
Signature				Date	9/1/00

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POLAR TOLANE LIQUID CRYSTALS

FIELD OF THE INVENTION

The present invention relates to liquid crystal materials and eutectic mixtures thereof. In particular, the invention is directed to a new class of polar asymmetric tolane derivatives and eutectic liquid crystal mixtures containing the derivatives with infrared and microwave applications.

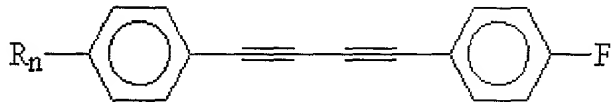
BACKGROUND OF THE INVENTION:

Liquid crystals that have high birefringence, low viscosity, and low threshold voltage, and are capable of maintaining a nematic phase over a broad temperature range are desirable in electro-optic phase and amplitude modulation applications. Such applications include infrared light valves, polymer-dispersed liquid crystals and cholesteric displays. High birefringence, or optical anisotropy (Δn), of the liquid crystal composition improves the efficiency of light modulation, and low rotational viscosity serves to shorten the response times. Low threshold voltage, which is inversely related to the dielectric anisotropy of the liquid crystal material, simplifies the electronics that drive the application.

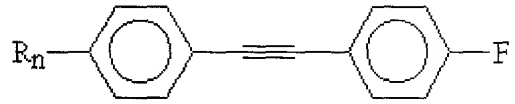
Polar liquid crystal compounds, particularly fluorinated species, have been investigated as possible candidates for such electro-optics applications. In general, fluorinated liquid crystal compounds have desirably low rotational viscosity, excellent photostability and

high resistivity. However, they also tend to exhibit modest dielectric anisotropy and, accordingly, high threshold voltage.

Increasing the asymmetry and, accordingly, the polarity of such compounds has been proposed as a means to improve the dielectric anisotropy of these compounds. Wu, et al. [Opt. Eng. 32, 1792-7 (1993)], for example, reported polar fluorinated diphenyldiacetylenes and tolanes as shown in Structures I and II below, respectively



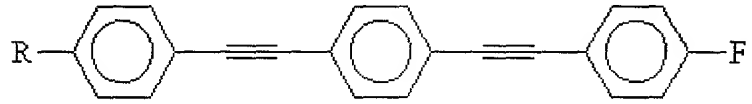
(Structure I)



(Structure II)

These compounds exhibit high birefringence, high resistivity, low viscosity, and comparatively low threshold voltage. However, while in some cases these compounds have reasonably low melting temperatures and heat fusion enthalpies, as is typical of compounds with high dipole moments, the melting temperature is too high and the nematic phase is too narrow.

The fluorination of polytolane liquid crystal compounds has also been investigated. In general, the highly conjugated polytolanes have desirably high birefringence. Fluorinated bis-tolanes such as shown in structure III, have been reported.

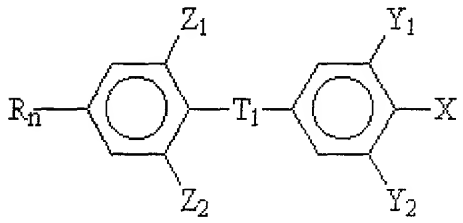


(Structure III)

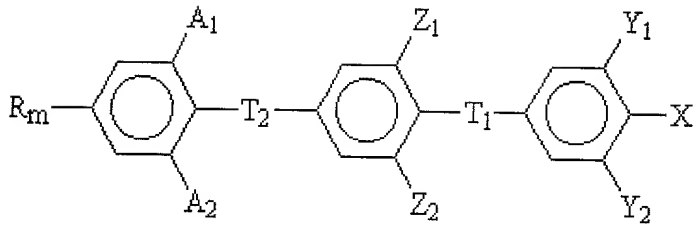
While this type of compound has good dielectric anisotropy, utility is limited, once again, due to high melting point and narrow nematic range.

SUMMARY OF THE INVENTION

A new class of liquid crystal compounds is provided which provides improved melting points and broader nematic ranges compared to previously reported fluorinated liquid crystal compounds. Specifically, the present invention provides a class of compounds based on the tolane and bis-tolane structures as shown in Structures IV and V.



(Structure IV)

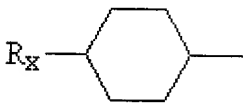


(Structure V)

For the compounds depicted in all of the above structures and described herein, a polar group such as F (fluoro), CN (cyano), OCF_3 (trifluoromethoxy), or NCS (isothiocyanate) is positioned at site X and fluoro groups are positioned at least one of the pairs of sites Y_1 and Y_2, Z_1 and Z_2, and for the bis-tolane derivatives, A_1 and A_2.

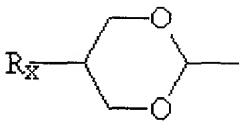
For the tolane derivatives as depicted in structure IV, T_1 is always a triple bond. For the bis-tolane derivatives, T_1 and T_2 are either both triple bonds or one of the two groups is a double bond with and the other remains a triple bond.

In this new class of compounds, R_n or R_m may be an alkyl group having the general formula C_nH_{2n+1}, an alkenyl group having the general formula C_nH_{2n-1}, an alkoxy group having the general formula OC_nH_{2n+1}, or an alkenoxy group having the general formula – OC_nH_{2n-1}. Additionally, for the tolane compounds depicted in structure IV, R_n may be a cyclohexyl substituent as shown in Structure VI



(Structure VI)

or a dioxane substituent as shown in Structure VII.



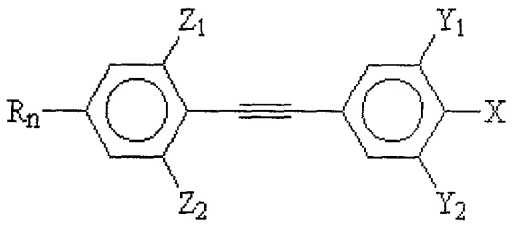
(Structure VII)

For both types of substituents, R_x may be an alkyl group having the general formula general formula $-C_xH_{2x+1}$, an alkenyl group having the general formula $-C_xH_{2x-1}$, an alkoxy group having the general formula $-OC_xH_{2x+1}$, or an alkenoxy group having the general formula $-OC_xH_{2x-1}$.

DETAILED DESCRIPTION OF THE INVENTION

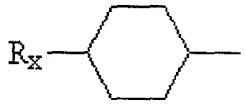
The present invention relates to a new class of liquid crystal materials and eutectic mixtures thereof and a method for their synthesis. It is anticipated that the invention may be tailored to a variety of other applications. The following description is presented to enable one of ordinary skill in the art to make and use the invention and to incorporate it in the context of particular applications. Various modifications, as well as a variety of uses in different applications, will be readily apparent to those skilled in the art, and the general principles defined herein may be applied to a wide range of embodiments. Thus, the present invention is not intended to be limited to the embodiments presented, but is to be accorded the widest scope consistent with the principles and novel features disclosed herein.

The present invention relates, generally, to fluorinated polar asymmetric liquid crystal compound, a method for their preparation, and their use in eutectic mixtures. In certain embodiments of this invention, tolane compounds are provided of the type depicted in Structure VIII:



(Structure VIII)

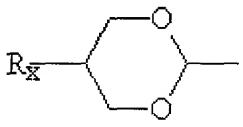
wherein X is a polar group such as F (fluoro), CN (cyano), OCF_3 (trifluoromethoxy), or NCS (isothiocyanate), and at least one of the pairs Y_1 and Y_2 and Z_1 and Z_2 are fluoro groups. In these embodiments, R_n may be an alkyl group having the general formula C_nH_{2n+1}, an alkenyl group having the general formula C_nH_{2n-1}, an alkoxy group having the general formula OC_nH_{2n+1}, or an alkenoxy group having the general formula OC_nH_{2n-1}. For these substituents, the value of n is preferably approximately 2 to 12. Additionally, R_n may be a substituent of the type shown in Structure VI,



(Structure VI)

wherein R_x is an alkyl group having the general formula C_xH_{2x+1}, an alkenyl group having the general formula C_xH_{2x-1}, an alkoxy group having the general formula

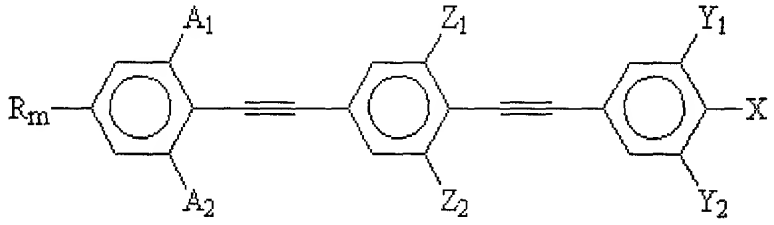
OC_xH_{2x+1}, or an alkenoxy group having the general formula OC_xH_{2x-1}. The value of x is preferably approximately 2 to 12. In yet another alternative, R_n may be a substituent of the type shown in Structure VII,



(Structure VII)

wherein again R_x may be an alkyl group having the general formula C_xH_{2x+1}, an alkenyl group having the general formula C_xH_{2x-1}, an alkoxy group having the general formula OC_xH_{2x+1}, or an alkenoxy group having the general formula OC_xH_{2x-1}. Again, the value of x is preferably approximately 2 to 12.

In other, preferred embodiments of this invention, bis-tolane compounds are provided as shown in structure IX,

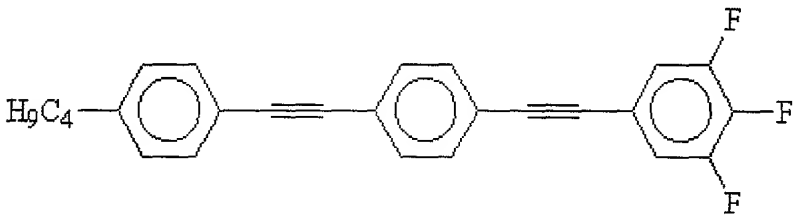


(Structure IX)

wherein X is a polar group such as F (fluoro), CN (cyano), OCF3(trifluoromethoxy), or NCS (isothiocyanate), and at least one of the pairs Y_1 and Y_2, Z_1 and Z_2, and A_1 and A_2 are fluoro groups. In this embodiment, R_m may be an alkyl group having the general formula C_mH_{2m+1}, an alkenyl group having the general formula C_mH_{2m-1}, an alkoxy group

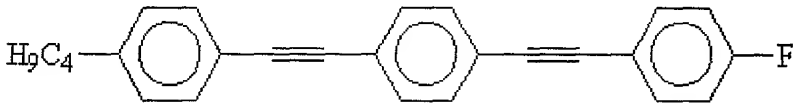
having the general formula OC_mH_{2m+1}, or an alkenoxy group having the general formula OC_mH_{2m-1}. The value of m is preferably approximately 2 to 12.

One example of this embodiment, wherein R_m is an alkyl group with m =4, is depicted for clarity in structure X and will henceforth be referred to as PTPTP-4FFF.



(Structure X)

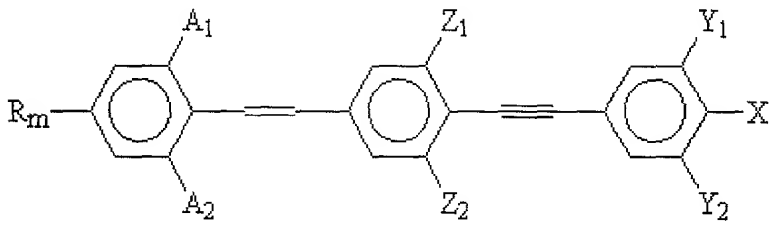
This trifluoro bis-tolane compound has a nematic range of 115 to 188.1 °C and a heat fusion enthalpy of 3.85 kcal/mol. In comparison, the monofluoro compound, henceforth referred to as PTPTP-4F, and depicted in structure XI,



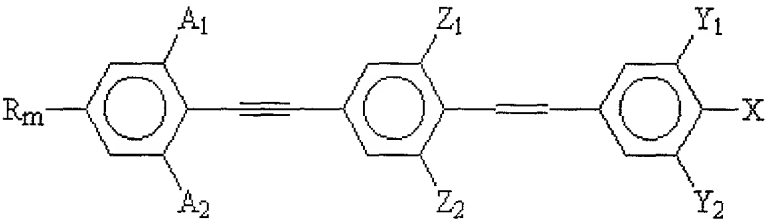
(Structure XI)

has a nematic range of 173.1 to 217.2 °C and a heat fusion enthalpy of 8.47 kcal/mol. The addition of the fluoro groups meta to the tolane triple bond serves to reduce both the melting and clearing points of the compound and accordingly reduce the heat fusion enthalpy. Further, in contrast to PTPTP-4F, the reduced melting point of the PTPTP-4FFF species renders it useful in eutectic mixtures.

In yet other embodiments, modified bis-tolane structures of the types depicted in Structures XII and XIII are provided:



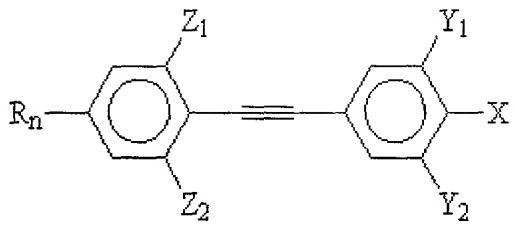
(Structure XII)



(Structure XIII)

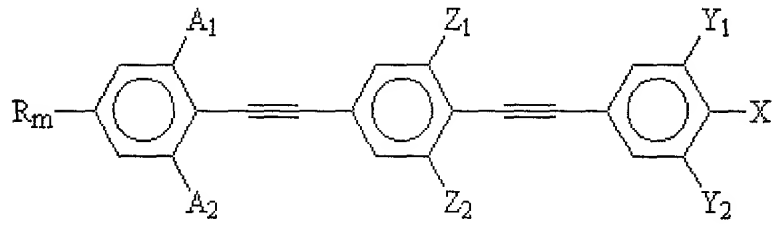
wherein X is a polar group such as F (fluoro), CN (cyano), OCF_3 (trifluoromethoxy), or NCS (isothiocyanate), and either the pair Y_1 and Y_2,the pair Z_1 and Z_2, or the pair A_1 and A_2 are fluoro groups and the alternate pairs are hydrogens. In this embodiment, R_m may be an alkyl group having the general formula C_mH_{2m+1}, an alkenyl group having the general formula C_mH_{2m-1}, an alkoxy group having the general formula OC_mH_{2m+1}, or an alkenoxy group having the general formula OC_mH_{2m-1}. The value of m is preferably approximately 2 to 12.

For preferred embodiments of the tolanes provided by the present invention as shown in structure VIII,

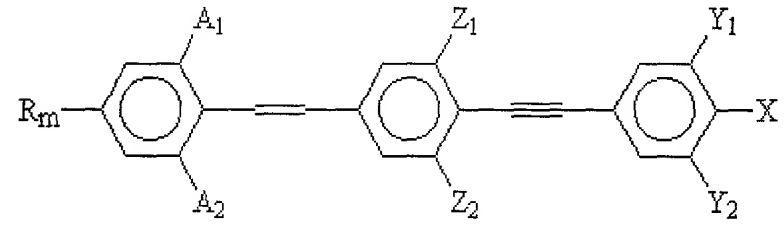


(Structure VIII)

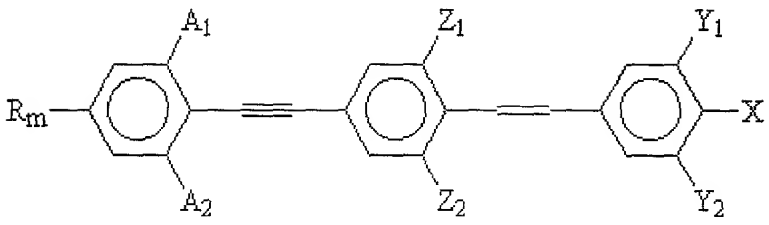
the R_n substituent is an alkenyl group having the general formula C_nH_{2n-1}, and more preferably an alkenyl group with the double bond in the second position and having the general formula $C_xH_{2x+1}CH=CH-CH_2-$. Similarly for the bis-tolanes and modified bis-tolane derivatives shown structures IX, XII, and XIII,



(Structure IX)



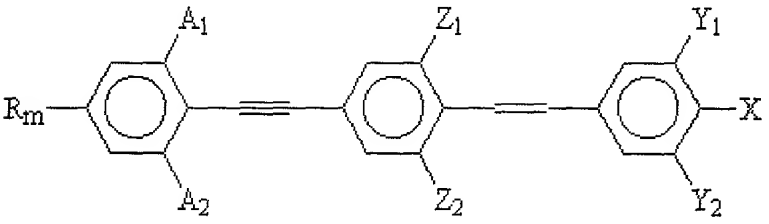
(Structure XII)



(Structure XIII)

R_m is preferably an alkenyl group with the general formula C_mH_{2m-1}, and more preferably an alkenyl with the double bond in the second position and having the general formula $C_xH_{2x+1}CH=CH-CH_2-$. Furthermore, for the tolanes, bis-tolanes, and modified bis-tolanes provided herein, fluoro substitution at the X, Y_1, and Y_2 positions is preferred.

Generally, the compounds provided in the present invention have large dipole moments that contribute to desirably high dielectric anisotropy. However, the positioning of the additional fluoro groups helps to reduce the high melting points characteristic of polar tolane and bis-tolane compounds. Modified bis-tolane structure XIII is shown here for reference.

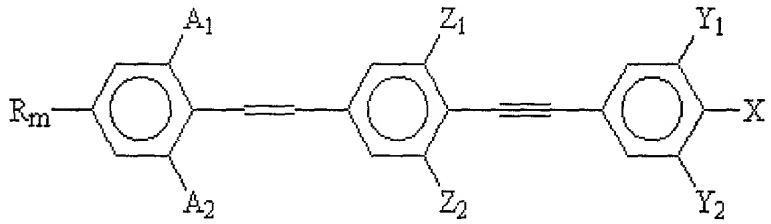


(Structure XIII)

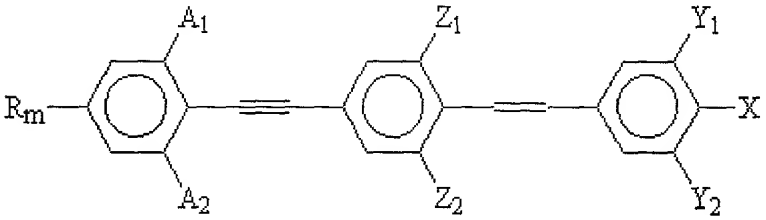
However, the principles presented herein apply to all embodiments of the present invention. It should be apparent to one skilled in the art that placing fluoro groups in at

least one pair of the Y_1, Y_2, or Z_1, Z_2, or A_1, A_2 paired positions in the above structure not only contributes to the overall dipole of the molecule but also serves to increase the effective molecular distance between molecules in the bulk phase. Increasing the intermolecular distance results in a decrease in melting point and heat fusion enthalpy.

For the modified bis-tolane embodiments of the present invention, reduction of one of the bis-tolane triple bonds to a double bond as shown in structures XII and XIII



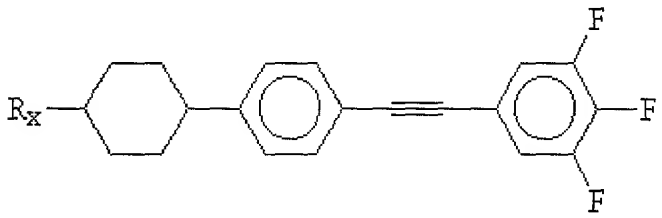
(Structure XII)



(Structure XIII)

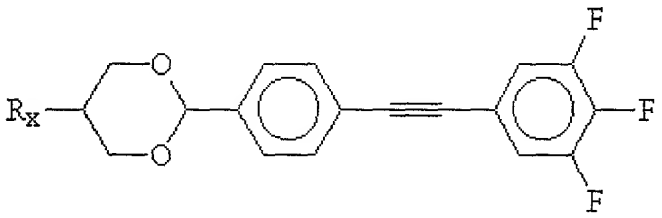
introduces a bend into the molecular structure. This bend, like the pairs of fluoro substituents, serves to increase the intermolecular distance in the bulk phase. Thus, the reduction of one of the triple bonds in the bis-tolane structure results in a lower melting point and heat fusion enthalpy for the compound.

In additional embodiments of the present invention, the compounds provided herein are utilized as components of eutectic mixtures. In general, compounds such as those depicted in structure XIV



(Structure IV)

are particularly effective due to low melting point and wide nematic range. Compounds such as PTPTP-4FFF and the class of compounds depicted in Structure XV,



(Structure XV)

while having relatively high melting points and limited nematic phases, are nonetheless useful as dopants for increasing the dielectric anisotropy of eutectic mixtures. Compounds of the type shown in structure XV, in particular, have very high dipole moments and accordingly large dielectric anisotropy values.

General procedures for the preparation of embodiments of this invention are provided in Schemes 1 and 2. Scheme 1 outlines particularly the synthesis of the tolane compounds

(**4**), and Scheme 2 outlines particularly the bis-tolane variants (**11**). A detailed description of a synthesis example compound PTPTP-4FFF according to Scheme 2 is provided below. It will be readily apparent to one skilled in the art that the synthesis for PTPTP-4FFF described herein can be readily adapted, as outlined in Schemes 1 and 2, to produce other variants of the present invention. Appropriate selection of reactants, such as substituted benzenes, as outlined in the Schemes below will provide the desired products according to the present invention.

To a mixture of (trimethylsilyl)acetylene **1a** (5.0 g, 51 mmol) and 1-butyl-4-iodobenzene **5** (10.6 g, 46 mmol) was added the catalyst system of $Pd(PPh_3)Cl_2$ (800 mg, 1.2 mmol) and CuI (220 mg, 1.2 mmol) followed by anhydrous tetrahydrofuran (50 mL). The mixture was kept under an Ar atmosphere and cooled with an ice-bath. Triethylamine (10 mL, 72 mmol) was added to the mixture through a syringe over 5 minutes and the orange solution was stirred for 1.5 hours while the ice-bath warmed up. The resulting dark solution was diluted with pentane and washed with 10% HCl, saturated $NaHCO_3$, and brine, successively. The organic layer was dried with Na_2SO_4, concentrated and passed through a plug of silica gel. Evaporation of solvent gave the trimethylsilyl acetylene derivative **6** as a clear oil (9.2 g, 100%).

To **6** (m = 4) (9.2 g, 46 mmol) was added a solution of NaOH (4 g, 100 mmol) in a mixed solvent of H_2O (8 mL), THF (8 mL) and MeOH (8 mL). The mixture was stirred at room temperature for 17 hours. It was then diluted with hexanes and washed with 10% HCl, saturated $NaHCO_3$ and brine, successively. The organic layer was dried with Na_2SO_4,

concentrated and passed through a plug of silica gel. Evaporation of solvent gave the unsubstituted acetylene compound **7** as a clear oil(5.5 g, 93%).

To an ice-bath-cooled mixture of **7** (m = 4) (1.88 g, 11.9 mmol), 1-bromo-4-iodobenzene 7a (3.06 g, 10.8 mmol), $Pd(PPh_3)Cl_2$ (209 mg, 0.3 mmol) and CuI (57 mg, 0.3 mmol) were added tetrahydrofuran (12 mL) followed by triethylamine (5 mL). The mixture was stirred for 24 hours at room temperature. The precipitates were removed by vacuum filtration and the filtrate was diluted with pentane. The organic layer was washed with 10% HCl, saturated $NaHCO_3$ and brine, successively. After drying with $MgSO_4$, concentration and filtration through silica gel, the brominated tolane **8** was obtained as a yellow solid (3.22 g, 95%).

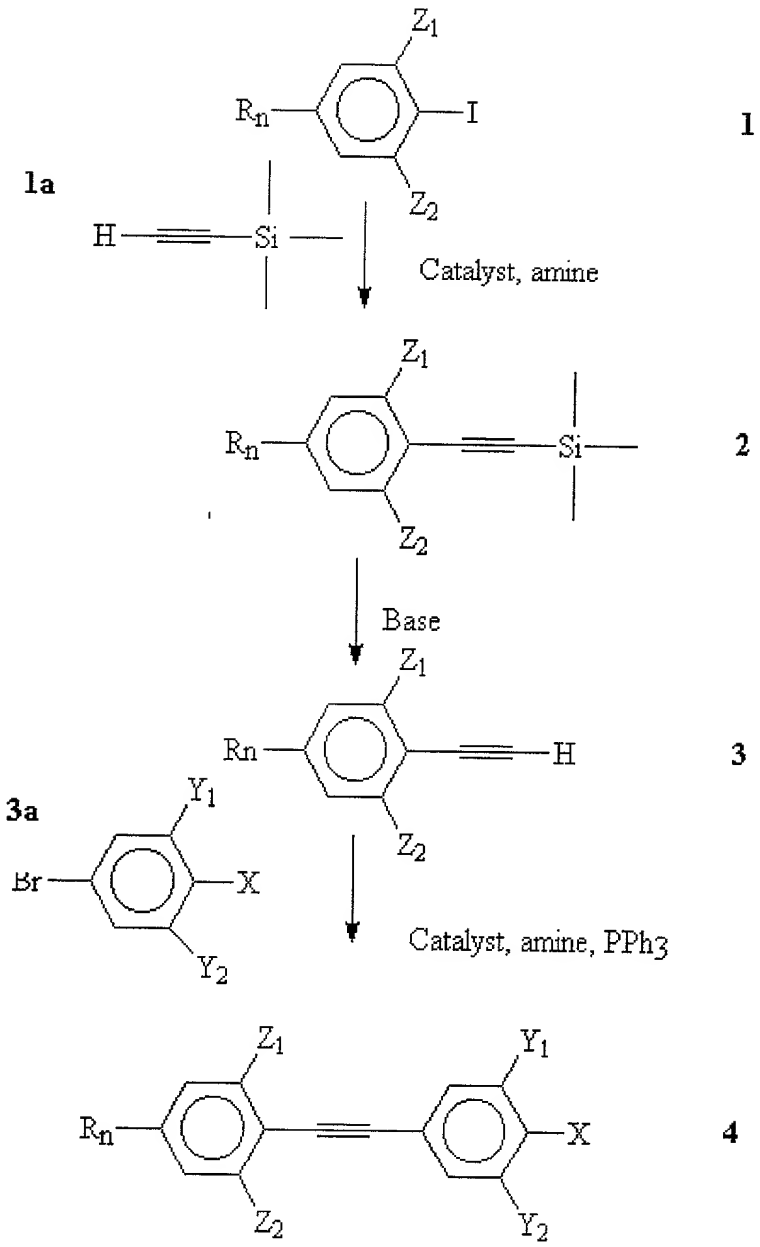
To a solution of **8** (m = 4) (743 mg, 2.4 mmol), $Pd(PPh_3)Cl_2$ (28 mg, 0.01 mmol), CuI (5 mg, 0.01 mmol) and PPh_3 (10 mg, 0.01 mmol) in triethylamine (10 mL) was added (trimethylsilyl)acetylene (500 μL, 3.6 mmol). The solution was refluxed under Ar for 1.5 hours and then cooled to room temperature. Hexane extracts of the mixture were washed with 10% HCl, saturated $NaHCO_3$, and brine, successively. The solution was dried with Na_2SO_4 and concentrated. The crude oil was subject to column chromatography to give a yellowish solid (604 mg, 84%) as the pure trimethylsilyl acetylene derivative **9**.

To a solution of **9** (m = 4) (430 mg, 1.3 mmol) in the mixed solvent of tetrahydrofuran (6 mL) and ethanol (6 mL) was added 1 g of Dowex® 550A OH^- anion-exchange resin.

The mixture was stirred at room temperature for 18 hours. After the resin was filtered, the solution was concentrated and filtered through silica gel (hexanes as eluent). Evaporation of solvent gave the unsubstituted acetylene derivative **10** as a yellow solid (350 mg, 100%).

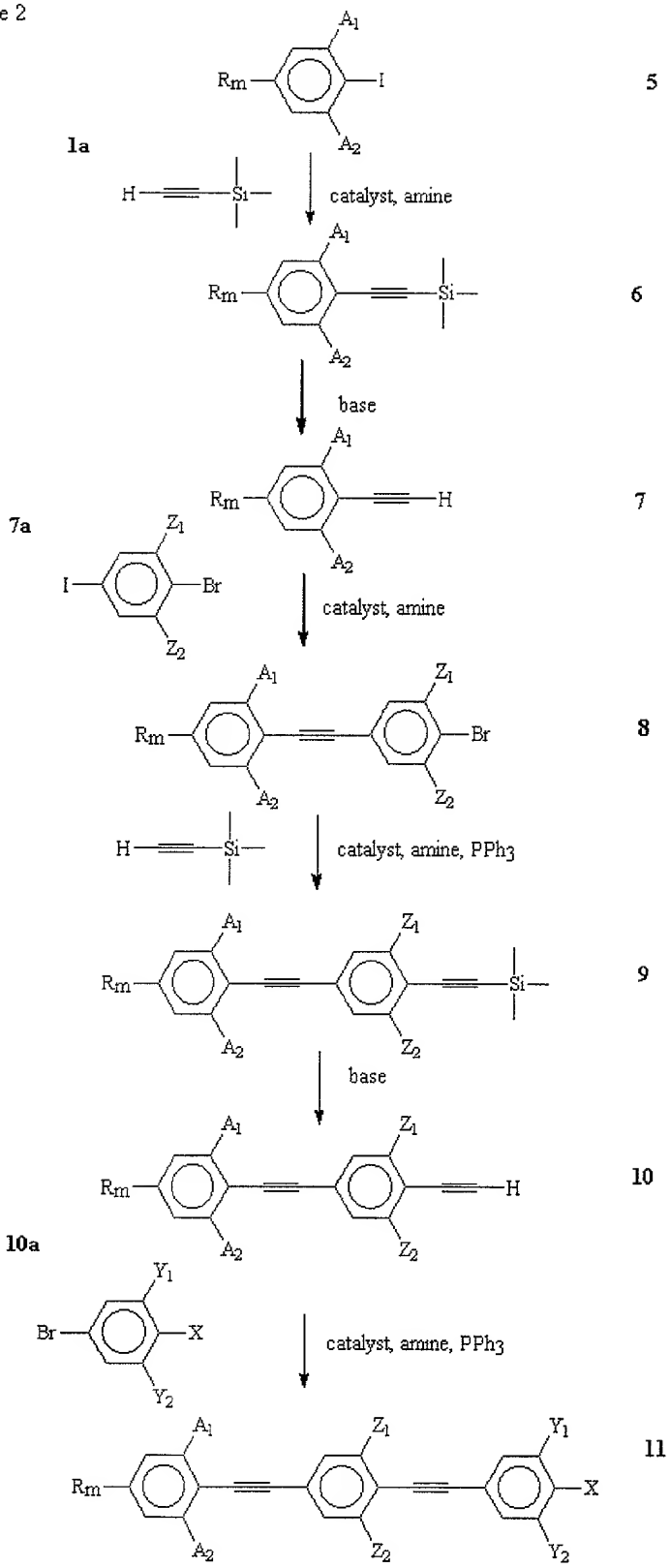
To a mixture of **10** (n = 4) (182 mg, 1 mmol) and 1-bromo-3,4,5-trifluorobenzene **10a** (211 mg, 1 mmol) was added $Pd(PPh_3)_4$ (12 mg, 0.01 mmol), CuI (2 mg, 0.01 mmol) and PPh_3 (4 mg, 0.01 mmol) followed by triethylamine (5 mL). The mixture was refluxed under Ar for 2 hours and cooled down to room temperature. It was then diluted with hexanes, filtered through silica gel and concentrated. Column chromatography of the crude oil gave the pure bis-tolane product **11** as a clear oil (80%).

Scheme 1


Z1
Rn
I
1
1a
H
Si
Z2
Catalyst, amine
Z1
Rn
Si
2
Z2
Base
Z1
Rn
H
3
Z2
3a
Y1
Br
X
Y2
Catalyst, amine, PPh3
Z1
Y1
Rn
X
4
Z2
Y2

5

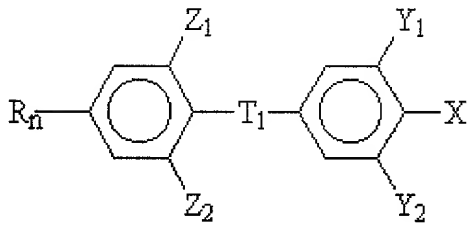
Scheme 2


5
1a
catalyst, amine
6
base
7
7a
catalyst, amine
8
catalyst, amine, PPh3
9
base
10
10a
catalyst, amine, PPh3
11

CLAIMS

What is claimed is:

1. Liquid crystal compounds having the general structure:



(Structure IV)

wherein X is selected from the group consisting of F (fluoro), CN (cyano), OCF_3(trifluoromethoxy), and NSC(isothiocyanate);

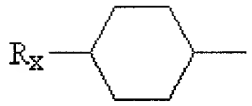
T_1 is a triple bond;

Y_1 and Y_2 are a pair of substituents selected from the group consisting of H and F, and $Y_1 = Y_2$;

Z_1 and Z_2 are a pair of substituents selected from the group consisting of H and F, and $Z_1 = Z_2$; and,

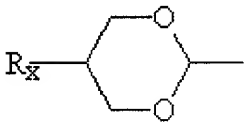
at least one of the pairs Y_1 and Y_2 and Z_1 and Z_2 are substituted with F;

Rn is selected from the group consisting of an alkyl group having the general formula C_nH_{2n+1}, an alkenyl group having the general formula C_nH_{2n-1}, an alkoxy group having the general formula OC_nH_{2n+1}, an alkenoxy group having the general formula OC_nH_{2n-1}, a group of the general structure



(Structure VI)

and a group of the general structure



(Structure VII)

wherein R_x for both structures is selected from a group consisting of an alkyl group having the general formula C_xH_{2x+1}, an alkenyl group having the general formula C_xH_{2x-1}, an alkoxy group having the general formula OC_xH_{2x+1}, and an alkenoxy group having the general formula OC_xH_{2x-1}.

2. A liquid crystal compound as set forth in claim **1**, wherein X is substituted with F; and, Y_1 and Y_2 are substituted with F and Z_1 and Z_2 are H groups.

3. A liquid crystal compound as set forth in claim **1**, wherein R_n is selected from a group consisting of an alkyl group having the general formula C_nH_{2n+1}, an alkenyl group having the general formula C_nH_{2n-1}, an alkoxy group having the general formula OC_nH_{2n+1}, and an alkenoxy group having the general formula OC_nH_{2n-1} where n is approximately 2 to 12.

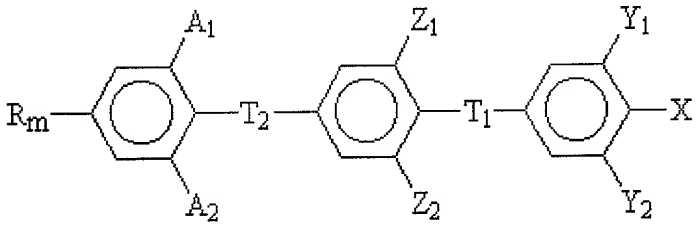
4. A liquid crystal compound as set forth in claim **1**, wherein R_x is selected from a group consisting of an alkyl group having the general formula C_xH_{2x+1}, an alkenyl group having the general formula C_xH_{2x-1}, an alkoxy group having the general formula OC_xH_{2x+1}, and an alkenoxy group having the general formula OC_xH_{2x-1} where x is approximately 2 to 12.

5. A liquid crystal compound as set forth in claim **1**, wherein R_n is an alkenyl group having the general formula C_nH_{2n-1}.

6. A liquid crystal compound as set forth in claim **1**, wherein R_n is an alkenyl group having the general formula C_nH_{2n-1} where n ranges approximately from 2 to 12.

7. A liquid crystal compound as set forth in claim **1**, wherein R_n is an alkenyl group having the general formula $C_xH_{2x-1}CH{=}CH\text{-}(CH_2)\text{-}$.

8. Liquid crystal compounds having the general structure



(Structure V)

wherein X is selected from the group consisting of F (fluoro), CN (cyano), OCF_3(trifluoromethoxy), and NSC(isothiocyanate);

T_1 is selected from the group consisting of a triple and a double covalent bond between two carbons;

T_2 is selected from the group consisting of a triple and a double covalent bond between two carbons; and,

T_1 is not equal to T_2 when T_1 or T_2 is a double bond;

Y_1 and Y_2 are a pair of substituents selected from the group consisting of H and F and $Y_1 = Y_2$;

Z_1 and Z_2 are a pair of substituents selected from the group consisting of H and F and $Z_1 = Z_2$;

A_1 and A_2 are a pair of substituents selected from the group consisting of H and F and $A_1 = A_2$;

at least one of the pairs Y_1 and Y_2, Z_1 and Z_2, and A_1 and A_2 is substituted with F; and,

R_m is selected from the group consisting of selected from a group consisting of an alkyl group having the general formula C_mH_{2m+1}, an alkenyl group having the general formula C_mH_{2m-1}, an alkoxy group having the general formula OC_mH_{2m+1}, and an alkenoxy group having the general formula OC_mH_{2m-1}.

9. A liquid crystal compound as set forth in claim **8**, wherein X is a substituted with F;

Y_1 and Y_2 are substituted with F; and,

Z_1 and Z_2 and A_1 and A_2 are H groups.

10. A liquid crystal compound as set forth in claim **8**, wherein T_1 and T_2 are triple bonds between two carbons.

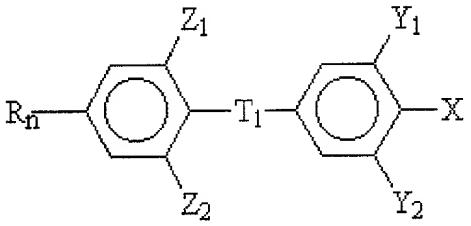
11. A liquid crystal compound as set forth in claim **8**, wherein R_m is selected from a group consisting of an alkyl group having the general formula C_mH_{2m+1}, an alkenyl group having the general formula C_mH_{2m-1}, an alkoxy group having the general formula OC_mH_{2m+1}, and an alkenoxy group having the general formula OC_mH_{2m-1} where m is approximately 2 to 12.

12. A liquid crystal compound as set forth in claim **8**, wherein R_m is an alkenyl group having the general formula C_mH_{2m-1}.

13. A liquid crystal compound as set forth in claim **8**, wherein R_m is an alkenyl group having the general formula C_mH_{2m-1} where m ranges approximately from 2 to 12.

14. A liquid crystal compound as set forth in claim **8**, wherein R_m is an alkenyl group having the general formula $C_mH_{2m-1}CH{=}CH\text{-}(CH_2)\text{-}$.

15. A eutectic mixture of liquid crystal compounds comprising at least two liquid crystal compounds, including at least one compound having the general structure



(Structure IV)

wherein X is selected from the group consisting of F (fluoro), CN (cyano), OCF3(trifluoromethoxy), and NSC(isothiocyanate);

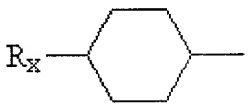
T_1 is a triple bond;

Y_1 and Y_2 are a pair of substituents selected from the group consisting of H and F and $Y_1 = Y_2$;

Z_1 and Z_2 are a pair of substituents selected from the group consisting of H and F and $Z_1 = Z_2$;

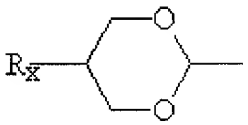
at least one of the pairs Y_1 and Y_2 and Z_1 and Z_2 are substituted with F;

R_n is selected from the group consisting of an alkyl group having the general formula C_nH_{2n+1}, an alkenyl group having the general formula C_nH_{2n-1}, an alkoxy group having the general formula OC_nH_{2n+1}, an alkenoxy group having the general formula OC_nH_{2n-1}, a group of the general structure



(Structure VI)

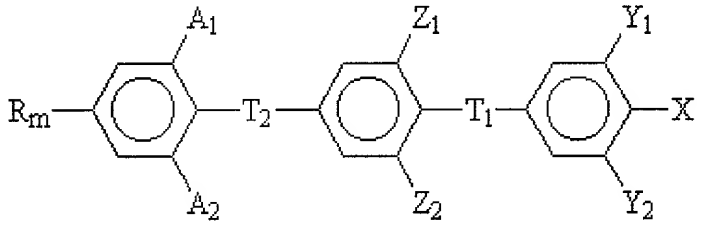
and a group of the general structure



(Structure VII)

wherein R_x for both structures is selected from a group consisting of an alkyl group having the general formula C_xH_{2x+1}, an alkenyl group having the general formula C_xH_{2x-1}, an alkoxy group having the general formula $-OC_xH_{2x+1}$, and an alkenoxy group having the general formula $-OC_xH_{2x-1}$.

16. A eutectic mixture of liquid crystal compounds comprising at least two liquid crystal compounds including at least one compound having the general structure



(Structure V)

wherein X is selected from the group consisting of F (fluoro), CN (cyano), OCF_3(trifluoromethoxy), and NSC(isothiocyanate);

T_1 is selected from the group consisting of a triple and a double covalent bond between two carbons;

T_2 is selected from the group consisting of a triple and a double covalent bond between two carbons; and,

T_1 is not equal to T_2 when T_1 or T_2 is a double bond;

Y_1 and Y_2 are a pair of substituents selected from the group consisting of H and F and $Y_1 = Y_2$;

Z_1 and Z_2 are a pair of substituents selected from the group consisting of H and F and $Z_1 = Z_2$;

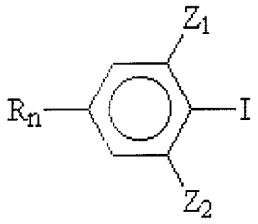
A_1 and A_2 are a pair of substituents selected from the group consisting of H and F and $A_1 = A_2$;

at least one of the pairs Y_1 and Y_2, Z_1 and Z_2, and A_1 and A_2 is substituted with F; and,

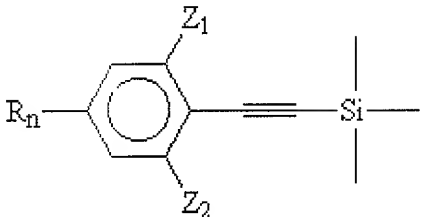
R_m is selected from the group consisting of selected from a group consisting of an alkyl group having the general formula C_mH_{2m+1}, an alkenyl group having the general formula C_mH_{2m-1}, an alkoxy group having the general formula OC_mH_{2m+1}, and an alkenoxy group having the general formula OC_mH_{2m-1}.

17. A method for preparing liquid crystal compounds, comprising the steps of:

a) reacting an iodobenzene as shown in Structure 1 with trimethylsilyl acetylene in the presence of a catalyst and an amine to produce an trimethylsilylacetyl derivative as shown in structure 2;



(Structure 1)

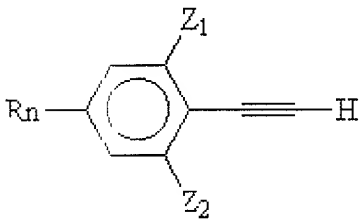


(Structure 2)

;

b) isolating the trimethylsilylacetyl derivative shown in structure 2 from the reaction of the iodobenzene shown in structure 1 and trimethylsilylacetylene in the presence of the catalyst and the amine;

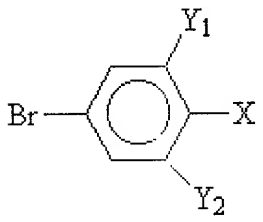
c) reacting the trimethylsilylacetyl derivative shown in structure 2 with a base to remove trimethyl silane and to give an unsubstituted product as shown in structure 3;



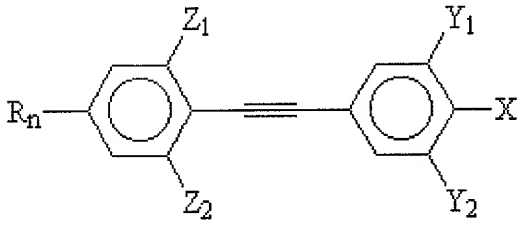
(Structure 3)

d) isolating the unsubstituted product as shown in structure 3 from the reaction of the trimethylsilylacetyl derivative shown in structure 2 with the base;

e) reacting the unsubstituted product as shown in structure 3 with a brominated, substituted benzene as shown in structure 3a to give a tolane product as shown in structure 4;



(Structure 3a)



(Structure 4)

f) isolating the tolane product shown in structure 4 from the reaction of the unsubstituted product as shown in structure 3 with the brominated, substituted benzene brominated, substituted benzene shown in structure 3a;

wherein X is selected from the group consisting of F (fluoro), CN (cyano), OCF_3(trifluoromethoxy), and NSC(isothiocyanate);

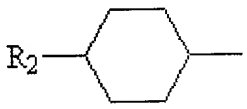
T_1 is a triple bond;

Y_1 and Y_2 are a pair of substituents selected from the group consisting of H and F, and $Y_1 = Y_2$;

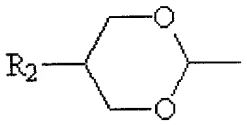
Z_1 and Z_2 are a pair of substituents selected from the group consisting of H and F, and $Z_1 = Z_2$; and,

At least one of the pairs Y_1 and Y_2 and Z_1 and Z_2 is substituted with F;

R_n is selected from the group consisting of an alkyl group having the general formula C_nH_{2n+1}, an alkenyl group having the general formula C_nH_{2n-1}, an alkoxy group having the general formula OC_nH_{2n+1}, an alkenoxy group having the general formula OC_nH_{2n-1}, a group of the general structure



and a group of the general structure



wherein R_x for both structures is selected from a group consisting of an alkyl group having the general formula C_xH_{2x+1}, an alkenyl group having the general formula C_xH_{2x-1}, an alkoxy group having the general formula OC_xH_{2x+1}, and an alkenoxy group having the general formula OC_xH_{2x-1}.

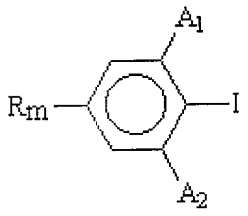
18. The method for preparing liquid crystal compounds as set forth in claim **17**, wherein the catalyst in steps a) and e) is $Pd(Ph_3)_2Cl_2/CuI$.

19. The method for preparing liquid crystal compounds as set forth in claim **17**, wherein the amine in steps a) and e) is triethylamine.

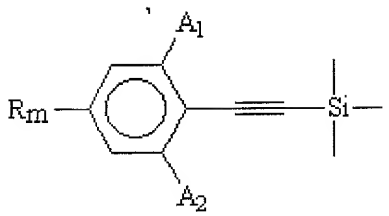
20. The method for preparing liquid crystal compounds as set forth in claim **17**, wherein the base in step c) is NaOH.

21. A method for preparing liquid crystal compounds, comprising the steps of:

a) reacting an iodobenzene as shown in Structure 5 with trimethylsilyl acetylene in the presence of a catalyst and an amine to produce an trimethylsilylacetyl derivative as shown in structure 6;



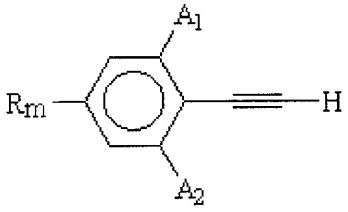
(Structure 5)



(Structure 6)

b) isolating the trimethylsilylacetyl derivative shown in structure 6 from the reaction of the iodobenzene shown in structure 5 and trimethylsilylacetylene in the present of the catalyst and the amine;

c) reacting the trimethylsilylacetyl derivative shown in structure 6 with a base to remove trimethyl silane and to give an unsubstituted product as shown in structure 7;

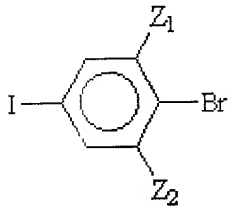


(Structure 7)

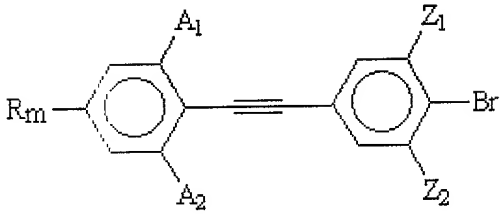
d) isolating the unsubstituted product as shown in structure 7 from the reaction of the trimethylsilylacetyl derivative shown in structure 6 with the base;

e) reacting the unsubstuted product as shown in structure 7 with a substituted bromoiodobenzene as shown in structure 7a in the presence of a catalyst, an

amine, and triphenylphosphine to prepare a brominated, substituted tolane product shown in structure 8;



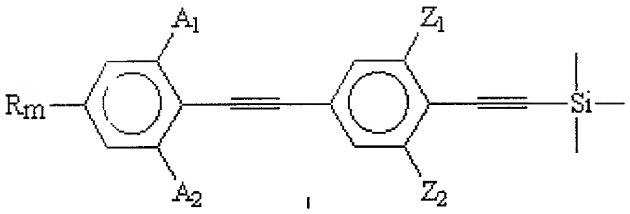
(Structure 7a)



(Structure 8)

f) isolating the brominated, substituted tolane product shown in structure 8 from the reaction of the unsubstuted product as shown in structure 7 with the substituted bromoiodobenzene as shown in structure 7a in the presence of the catalyst, the amine, and triphenylphosphine;

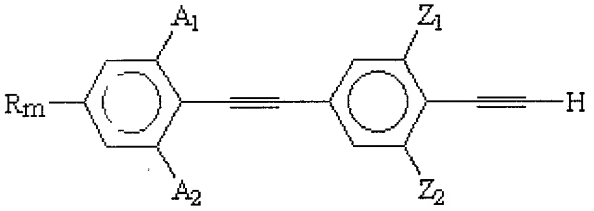
g) reacting the brominated, substituted tolane product shown in structure 8 with trimethylsilylacetylene in the presence of the catalyst, the amine, and triphenylphosphine to produce a trimethylacetyl derivative as shown in structure 9;



(Structure 9)

h) isolating the trimethylacetyl derivative shown in structure 9 from the reaction of the brominated, substituted tolane product shown in structure 8 with trimethylsilylacetylene in the presence of the catalyst, the amine, and triphenylphosphine;

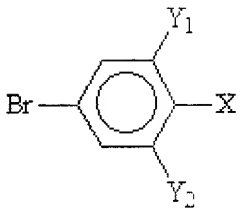
i) reacting the trimethylsilylacetyl derivative shown in structure 9 with a base to remove trimethylsilane and produce an unsubstituted product as shown in structure 10;



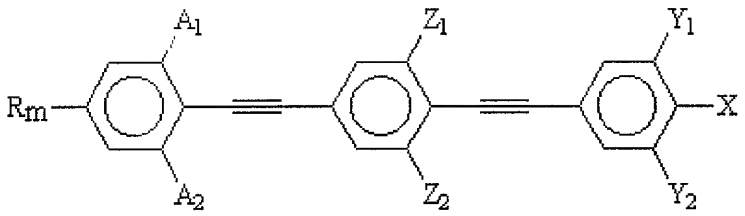
(Structure 10)

j) isolating the unsubstituted product shown in structure 10 from the reaction of the trimethylsilyl derivative shown in structure 9 with the base;

k) reacting the unsubstituted product shown in structure 10 with a substituted bromobenzene as shown in structure 10a in the presence of a catalyst, an amine, and triphenylphosphine to produce a bis-tolane product as shown in structure 11;



(Structure 10a)



(Structure 11)

l) isolating the bis-tolane product shown in structure 11 from the reaction of the unsubstituted product shown in structure 10 with the substituted bromobenzene shown in structure 10a in the presence of the catalyst, the amine, and triphenylphosphine;

wherein for the structures shown, X is selected from the group consisting of F (fluoro), CN (cyano), OCF_3(trifluoromethoxy), and NSC(isothiocyanate);

T_1 is selected from the group consisting of a triple and a double covalent bond between two carbons;

T_2 is selected from the group consisting of a triple and a double covalent bond between two carbons; and,

T_1 is not equal to T_2 when T_1 or T_2 is a double bond;

Y_1 and Y_2 are a pair of substituents selected from the group consisting of H and F and $Y_1 = Y_2$;

Z_1 and Z_2 are a pair of substituents selected from the group consisting of H and F and $Z_1 = Z_2$;

A_1 and A_2 are a pair of substituents selected from the group consisting of H and F and $A_1 = A_2$;

at least one of the pairs Y_1 and Y_2, Z_1 and Z_2, and A_1 and A_2 is substituted with F; and,

R_m is selected from the group consisting of selected from a group consisting of an alkyl group having the general formula C_mH_{2m+1}, an alkenyl group having the general formula C_mH_{2m-1}, an alkoxy group having the general formula OC_mH_{2m+1}, and an alkenoxy group having the general formula OC_mH_{2m-1}.

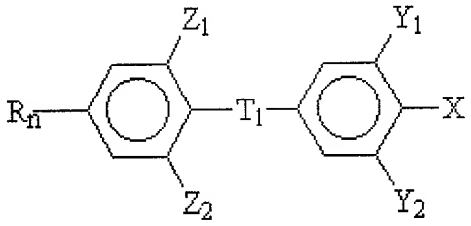
22. The method for preparing liquid crystal compounds as set forth in claim **21**, wherein the catalyst in steps a), e), g), and k) is $Pd(Ph_3)_2Cl_2/CuI$.

23. The method for preparing liquid crystal compounds as set forth in claim **21**, wherein the amine in steps a), e), g), and k) is triethylamine.

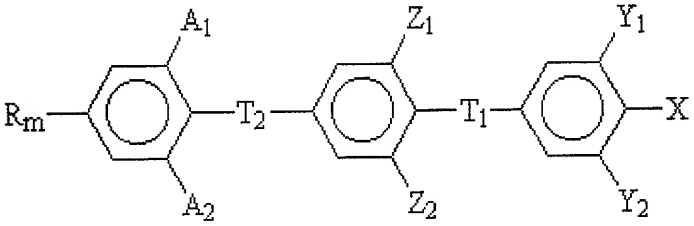
24. The method for preparing liquid crystal compounds as set forth in claim **21**, wherein the base in steps c) and i) is NaOH.

ABSTRACT

A new class of liquid crystal compounds is based on tolane and bis-tolane structures:



(Structure IV)

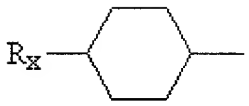


(Structure V)

in which X is a polar group such as F (fluoro), CN (cyano), OCF_3 (trifluoromethoxy), or NCS (isothiocyanate) at least one of the pairs of sites Y_1 and Y_2, Z_1 and Z_2, and for the bis-tolane derivatives, A_1 and A_2 are fluoro groups.

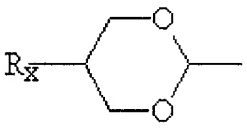
T_1 for the tolane derivatives is always a triple bond. For the bis-tolane derivatives, T_1 and T_2 are either both triple bonds or one of the two groups is a double bond with and the other remains a triple bond.

R_n or R_m may be an alkyl group having the general formula C_nH_{2n+1}, an alkenyl group having the general formula C_nH_{2n-1}, an alkoxy group having the general formula OC_nH_{2n+1}, or an alkenoxy group having the general formula $-OC_nH_{2n-1}$. Additionally, for the tolane compounds, R_n may be a cyclohexyl substituent:



(Structure VI)

or a dioxane substituent:



(Structure VII)

in which R_x is an alkyl group having the general formula general formula C_xH_{2x+1}, an alkenyl group having the general formula C_xH_{2x-1}, an alkoxy group having the general formula OC_xH_{2x+1}, or an alkenoxy group having the general formula OC_xH_{2x-1}.

These compounds exhibit useful nematic ranges and melting points. Also disclosed are eutectic mixtures including these compounds.

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DECLARATION FOR UTILITY OR DESIGN PATENT APPLICATION (37 CFR 1.63)

☒ Declaration Submitted with Initial Filing OR ☐ Declaration Submitted after Initial Filing (surcharge (37 CFR 1.16 (e)) required)

Attorney Docket Number	HRL033B
First Named Inventor	Shin-Tson Wu
COMPLETE IF KNOWN	
Application Number	/
Filing Date	
Group Art Unit	
Examiner Name	

As a below named inventor, I hereby declare that:

My residence, post office address, and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled.

Polar Tolane Liquid Crystals

(Title of the Invention)

the specification of which
☒ is attached hereto
OR
☐ was filed on (MM/DD/YYYY) _____ as United States Application Number or PCT International Application Number _____ and was amended on (MM/DD/YYYY) _____ (if applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment specifically referred to above

I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR 1 56

I hereby claim foreign priority benefits under 35 U.S.C. 119(a)-(d) or 365(b) of any foreign application(s) for patent or inventor's certificate, or 365(a) of any PCT international application which designated at least one country other than the United States of America, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or of any PCT international application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application Number(s)	Country	Foreign Filing Date (MM/DD/YYYY)	Priority Not Claimed	Certified Copy Attached? YES	NO
			☐	☐	☐
			☐	☐	☐
			☐	☐	☐
			☐	☐	☐

☐ Additional foreign application numbers are listed on a supplemental priority data sheet PTO/SB/02B attached hereto:

I hereby claim the benefit under 35 U S.C. 119(e) of any United States provisional application(s) listed below.

Application Number(s)	Filing Date (MM/DD/YYYY)

☐ Additional provisional application numbers are listed on a supplemental priority data sheet PTO/SB/02B attached hereto.

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DECLARATION — Utility or Design Patent Application

I hereby claim the benefit under 35 U.S.C. 120 of any United States application(s), or 365(c) of any PCT international application designating the United States of America, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U S.C. 112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR 1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application.

U.S. Parent Application or PCT Parent Number	Parent Filing Date (MM/DD/YYYY)	Parent Patent Number *(if applicable)*

☐ Additional U.S. or PCT international application numbers are listed on a supplemental priority data sheet PTO/SB/02B attached hereto.

As a named inventor, I hereby appoint the following registered practitioner(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith. ☐ Customer Number [ ] → *Place Customer Number Bar Code Label here*

OR

☒ Registered practitioner(s) name/registration number listed below

Name	Registration Number	Name	Registration Number
Cary Tope-McKay	41,350		

☐ Additional registered practitioner(s) named on supplemental Registered Practitioner Information sheet PTO/SB/02C attached hereto.

Direct all correspondence to: ☐ Customer Number or Bar Code Label [ ] *OR* ☒ Correspondence address below

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true, and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under 18 U.S.C 1001 and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Name of Sole or First Inventor: ☐ A petition has been filed for this unsigned inventor

Given Name (first and middle [if any])	Family Name or Surname
Shin-Tson	Wu

Inventor's Signature	Shin-Tson Wu					Date	8/30/00
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☒ Additional inventors are being named on the 2 supplemental Additional Inventor(s) sheet(s) PTO/SB/02A attached hereto

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Supplemental Sheet
Page 1 of 2

Name of Additional Joint Inventor, if any:	☐ A petition has been filed for this unsigned inventor						
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Inventor's Signature						**Date**	
Residence: City		**State**		**Country**		**Citizenship**	
Post Office Address							
Post Office Address							
City		**State**		**ZIP**		**Country**	

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Given Name (first and middle [if any])			Family Name or Surname				
Inventor's Signature						**Date**	
Residence: City		**State**		**Country**		**Citizenship**	
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Page 2 of 2

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Name of Additional Joint Inventor, if any: ☐ A petition has been filed for this unsigned inventor

Given Name (first and middle [if any])	Family Name or Surname

Inventor's Signature						Date	
Residence: City		State		Country		Citizenship	
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Name of Additional Joint Inventor, if any: ☐ A petition has been filed for this unsigned inventor

Given Name (first and middle [if any])	Family Name or Surname

Inventor's Signature						Date	
Residence: City		State		Country		Citizenship	
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